

CHARACTERIZATION OF THE ACIDITY OF Al- AND Zr-PILLARED CLAYS

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Abstract—The surface acidic properties of pillared clays (PILCs) with Al or Zr oxide pillars (prepared from a natural Portuguese smectite and a synthetic Laponite), and of a protonic NaHY zeolite, were studied by two methods: pyridine adsorption followed by infrared (IR) spectroscopy, and the catalytic transformation of 1-butene. The results of the pyridine adsorption revealed that all the pillared clays studied have mainly Lewis-type acidity, the exception being the clay pillared with Zr oxide, obtained from natural smectite, which also presents a significant number of Brønsted acid sites. The results of 1-butene transformation showed that the pillared clays exhibit catalytic properties similar to those of the protonic Y zeolite. The acid character of the solids was confirmed by the values of the *cis/trans* 2-butene isomers ratio. At short reaction times, product distribution showed that the main reaction is oligomerization, followed by cracking. After 15 min the products are mainly the linear isomers, *cis* and *trans*-2-butene, showing that the majority of the catalytic active sites, are already poisoned after 15 min of reaction. The particular behaviour of Laponite intercalated with Al oxide pillars is discussed. The IR spectra of the pyridine adsorbed on the fresh samples and after the catalytic assays, revealed that Lewis acid sites behave as active sites for 1-butene catalytic transformation. The consistency between the results of the two complementary techniques used for the characterization of the acidity of the solids was proved.

Key Words—Acidity, 1-butene Transformation, Pillared Clays, Pyridine Adsorption, Y Zeolite.

INTRODUCTION

Pillared clays (PILCs) are porous materials obtained by intercalation with bulky polyoxocations of swelling clays, mainly montmorillonites. After calcination at temperatures usually in the range 350–500°C, the intercalated polyoxocations are transformed into rigid oxide pillars, giving pillared clays. Review of the first 10 years of research concerning the preparation of pillared clays (Vaughan, 1988) showed that the main objective of the various studies performed was to obtain acid solids with large pores that could be competitive with the protonic Y zeolite. To increase the dimensions of the pores in catalysts was, at that time, a very important research area, as the processing of lower-quality crude oils became important. With this in mind, the intention was to obtain pillared clays with properties as similar as possible to those of the faujasitic structure. On the other hand, Al solution chemistry was known well and inorganic polyoxocations with the Keggin-like Al_{13}^{7+} structure were the first intercalating agents used. The lack of thermal stability of the pillared clays obtained at the time were the main drawback for their use as cracking catalysts. In fact, the regeneration conditions to which cracking catalysts are submitted cause irreversible damage to the PILC structures. Recent studies concern-

ing pillared clays had two main objectives: (1) increasing pillared clay thermal stability; and (2) finding new applications for these materials. Thus, several pillar compositions, of pure or mixed oxides of, *e.g.* Al, Zr, Al/Ce, Al/Ga and Al/Fe (Auer and Hofmann, 1993; Brotas de Carvalho *et al.*, 1996; Ladavos *et al.*, 1996; Flego *et al.*, 1998; Pires *et al.*, 1998a), have been tested. At the same time, promising new uses for these materials have been explored, *e.g.* as adsorbents (Malla and Komarneni, 1990; Pereira *et al.*, 1998; Pires *et al.*, 2001), or as catalysts for reactions demanding mild acid and temperature conditions (Molina *et al.*, 1994; Benito *et al.*, 1999). The literature related to this increasing research field was reviewed recently by Lambert and Poncelet (1997) and Gil *et al.* (2000).

The present study focuses on the characterization of the surface acidity of PILCs with Al or Zr oxide pillars (prepared from a natural Portuguese smectite and a synthetic Laponite), and a protonic Y zeolite. The techniques used were pyridine adsorption followed by IR spectroscopy, and 1-butene transformation. These complementary techniques will allow us to establish the type, strength and density of the acid centers.

The adsorption of bases followed by IR spectroscopy is a commonly used method for characterization of the acidity of solids (Guiu and Grange, 1997; Geatti *et al.*, 1997; Pires *et al.*, 1998b; Raimond *et al.*, 1998) and its great advantage is the identification of the type of acid sites present, also allowing a semi-quantitative evaluation of their strength.

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The choice of 1-butene catalytic transformation as the model reaction for the characterization of the acidity of solids is based on the reactions of alkenes with acid solids reported in the literature (Medema, 1975; Tsuchiya *et al.*, 1987; Araya *et al.*, 1992; Geatti *et al.*, 1997; Costa *et al.*, 1999). It is well known that the transformation of alkenes is not a very demanding reaction with respect to acidity and temperature, allowing important conclusions about the solids used as catalysts. In fact, through the reaction distribution products, one can investigate the influence of the porous structure, as well as the acid/basic nature of the solids, using for that the *cis/trans* isomers ratio, as is reported in the literature (Perot *et al.*, 1976; Guisnet *et al.*, 1977; Costa *et al.*, 1999).

EXPERIMENTAL

Materials

The pillared clays used in this study were prepared from a natural smectite clay from a soil deposit at Benavila (Alentejo, Portugal), and from a commercial hectorite-type clay, Laponite, supplied by Laporte Industries (UK).

The complete characterization of the natural Portuguese clay, obtained after removing carbonates and subsequent sedimentation of a representative soil sample, was performed in a previous work (Brotas de Carvalho *et al.*, 1996) and is described in detail in Pires *et al.* (2000a). Briefly, this sample, primarily montmorillonite, has the structural formula ${}^{\text{IV}}(\text{Si}_{3.77}\text{Al}_{0.23}){}^{\text{VI}}(\text{Al}_{1.13}\text{Fe}_{0.47}\text{Mg}_{0.50})(\text{Ca}/2,\text{K},\text{Na})_{0.46}$, (following Weaver and Pollard, 1975). Its specific surface area, A_{BET} , obtained from N_2 adsorption at -196°C data is $49\text{ m}^2\text{ g}^{-1}$ and its d_{001} value is 1.50 nm.

The starting Laponite has an A_{BET} value of $347\text{ m}^2\text{ g}^{-1}$ and, as indicated by the supplier, its structural formula is ${}^{\text{IV}}(\text{Si}_4){}^{\text{VI}}(\text{Mg}_{2.75}\text{Li}_{0.15})(\text{Na})_{0.35}$. Regarding the d_{001} value, no result could be obtained as the X-ray diffraction (XRD) pattern obtained with this sample presents a very broad peak which prevents an accurate determination. This was also found by other authors (Occelli *et al.*, 1984; Cool and Vansant, 1996), and is attributed to the small dimensions of the crystals (nm in scale). These small dimensions favor the edge-to-face and the edge-to-edge association of the particles and so practically no regularity in the stacking is observed, and thus the XRD pattern is similar to that of an X-ray amorphous material.

Synthesis of the pillared clays

The pillaring processes used to introduce Al or Zr oxide pillars were optimized in previous studies (Brotas de Carvalho *et al.*, 1996; Pereira *et al.*, 1998; Pires *et al.*, 1997). In the present work, the smectite used for the pillaring process was obtained after removing the carbonates from the natural soil sample, *i.e.* no

sedimentation was performed. In fact, pillaring experiments conducted on samples obtained before and after sedimentation of this natural smectite (Pires *et al.*, 2000b) proved that there is no difference in d_{001} values and only a minor difference in A_{BET} values (4% larger for sedimented samples). So, for this natural smectite, the elimination of the time-consuming sedimentation process does not affect the characteristics of the pillared samples and reduces the synthesis time significantly.

The pillaring protocols established after a systematic study of several sets of experimental conditions that have a strong influence on the A_{BET} and the d_{001} of the synthesized materials are summarized briefly in the following. To prepare Al oxide pillared clays the oligomer solution, with OH/Al ratio = 2, was prepared from solutions of AlCl_3 (0.5 M) and NaOH (0.2 M). After mixing, it was aged for 2 h at 60°C and overnight at room temperature, after which the pH was increased to 6, by addition of a 25% NH_4OH solution. The oligomer solution was added dropwise to an aqueous clay suspension (5 g/L stirred overnight at room temperature) at 80°C under stirring, refluxed for 3 h at this temperature, and maintained overnight at 25°C . The solid was recovered by centrifugation and washed in a dialysis tube until the conductivity was $<1\text{ mS m}^{-1}$. The samples were then freeze dried and heated under a flow of dry air at 350°C for 2 h. The amounts of Al_2O_3 , determined elsewhere, (Pires *et al.*, 1997) by atomic absorption spectroscopy (AAS), were 15.9 and 36.7%, for the initial clay (BEN), and for the pillared sample (Al-BEN), respectively.

To obtain the Zr oxide pillared clays the pillaring process began with the slow addition of an aqueous solution of ZrOCl_2 (0.1 M) to a suspension of 1 g of clay in 100 mL of water, continuously stirred. The Zr/clay ratio was 2.5 mmol/g. The reaction occurred for 2 h at 40°C , after which the suspension was centrifuged, and the solid was successively washed, freeze dried and finally heated as were the Al-pillared clays. This procedure allowed 10.8% of ZrO_2 into the PILC, as determined by AAS. It was noticed that, although reducing the ZrO_2 amount to 6.4% gave a concomitant surface area decrease to $164\text{ m}^2\text{ g}^{-1}$, increasing the ZrO_2 content from 10.8 to 14.0% did not necessarily lead to an increase of the surface area. Therefore, the sample with 10.8% was chosen for this study.

In the text, the samples are referred to by the type of pillar (Al or Zr) followed by LAP or BEN for Laponite or natural smectite (from Benavila), respectively.

Protonic form of Y zeolite

A protonic form of Y zeolite was used for comparison. This sample was obtained from a Na form of zeolite Y (Aldrich Lot. 03910KG) that was submitted to three ion exchanges with a solution of NH_4NO_3 (2 M). The exchanges were performed at room temperature and using a relation between the volume of solution and the

amount of solid of 20 mL/g. After these treatments the solid was washed, dried and finally heated, under N₂ flow, at 400°C for 4 h. The material thus obtained has ~75% of the initial Na⁺ cations exchanged by protons, and will henceforth be referred to as NaHY zeolite. We do not need a greater protonic density for this zeolite because it is known that olefin transformation on acid catalysts is not a very demanding reaction as far as acidity is concerned (Medema, 1975; Tsuchiya *et al.*, 1987; Araya *et al.*, 1992; Geatti *et al.*, 1997).

X-ray diffraction

X-ray diffraction patterns of parent and modified clays were obtained on oriented mineral aggregates in a Philips PX 1820 diffractometer using CuK α radiation. To prepare the oriented films, the pillared clays were dispersed in distilled water under ultrasonication (5 min at room temperature), deposited on glass slides and allowed to evaporate.

Nitrogen adsorption

Nitrogen adsorption isotherms at -196°C were determined either in an automatic apparatus (Omnisorp, 100Cx from Coulter USA) or in a conventional, pyrex, volumetric apparatus, equipped with a pressure transducer (MKS-Baratron 0-133 kPa). To assure a clean surface, before the adsorption measurements, the samples were submitted to outgassing under vacuum <10⁻² Pa (10⁻⁴ Torr) with a linear increase in temperature of 5°C/min from ambient temperature to 300°C and then held for 2 h at this temperature. As demonstrated in previous works (Brotas de Carvalho *et al.*, 1996; Pereira *et al.*, 1998) no changes in the adsorption data were observed when longer outgassing times were used.

The A_{BET} values were estimated by applying the BET equation to the adsorption data and using 0.162 nm² for the cross-sectional area of the adsorbed N₂ molecule.

Infrared spectroscopy of adsorbed pyridine

Infrared spectra were obtained at room temperature using a Perkin-Elmer 1725 X FTIR spectrometer. Self-supported wafers of the pillared clays and the NaHY zeolite were placed in an IR cell which has NaCl windows and a heating zone which allows the initial outgassing of the wafers at 300°C for 2 h under vacuum <10⁻² Pa. After this activation treatment the wafers were cooled to ambient temperature and saturated with pyridine (C₅H₅N) by exposition to pyridine vapor for 20 min. After removal of the physisorbed pyridine and outgassing of the wafers for 10 h under the vacuum produced by a rotary pump, the spectra of the chemically adsorbed pyridine was collected. The samples were then successively outgassed for 1.5 h at 200, 300 and 400°C, under a vacuum of <10⁻² Pa. After each heat treatment the samples were cooled to room temperature and their IR spectra were registered.

Deactivated samples obtained after the catalytic tests performed at 300°C (described below) were also submitted to pyridine adsorption. In this case the self-supported wafers were placed in the IR cell and saturated directly with pyridine using the same experimental process as described previously. After removing the excess pyridine the IR spectra were collected.

Catalytic 1-butene transformation

Catalytic 1-butene (H₂C=CH-CH₂-CH₃) transformation tests were performed at atmospheric pressure in a dynamic vertical fixed-bed glass reactor having in its lower part a porous plate to support the catalyst and in its central part a thermometric wheel in which a Ni-chromonickel thermopar is introduced, to allow the control of the catalyst temperature. The reactor is maintained in a vertical tubular oven with thermal regulation by a programmer-controller (Shimaden FP 21, Japan). 100 mg of each sample were used in all the tests, and the catalytic bed was maintained at a uniform height, to avoid preferential paths.

Before the reactant was fed to the reactor, all the samples were pre-treated *in situ* at 350°C for 12 h under a constant flow of dry N₂ to obtain a clean surface and to assure that the dehydroxylation, which corresponds to the conversion of Brønsted into Lewis acid sites, occurs to the same extent for all of the samples. Experiments were performed at 130°C for 80 min, and at 200 and 300°C for 15 min, always using a flow of reactant (5% 1-butene in N₂) of 20 mL/min. Samples of the effluent (unconverted 1-butene and the reaction products) were injected into a gas chromatograph (Perkin Elmer-Auto System, USA) equipped with a 50 m PLOT/Al₂O₃-KCl column through an automatic six-door gauge. The chromatograph was equipped with a flame ionization detector (FID) and the peak areas as well as the mass percent of each reaction product were obtained directly with an integrator (PE Nelson Model 1020, USA).

To ensure the reproducibility of the data obtained, several catalytic tests were performed more than once, in the same experimental conditions. Control experiments were also carried out under the same experimental conditions, but in the absence of a catalyst, and no products of thermal transformation were detected.

RESULTS AND DISCUSSION

Textural properties

In Table 1 the *d* values of the pillared clays obtained from the BEN parent clay are presented. For Al-LAP no value is indicated since, as was already mentioned, its particle size, prevents an accurate determination of *d*₀₀₁.

Figure 1 displays the results of N₂ adsorption at -196°C for Al-LAP only, as the isotherms obtained for Al-BEN and Zr-BEN have already been published and discussed elsewhere (Brotas de Carvalho *et al.*, 1996; Pereira *et al.*, 1998; Pires *et al.*, 2000a). The configuration

Table 1. d values, specific surface area (A_{BET}) and microporous (V_{micro}) and mesoporous (V_{meso}) volumes, obtained from nitrogen adsorption at -196°C , for the pillared clays.

	d_{001} (nm)	A_{BET} ($\text{m}^2 \text{g}^{-1}$)	V_{micro}^1 ($\text{cm}^3 \text{g}^{-1}$)	V_{meso}^2 ($\text{cm}^3 \text{g}^{-1}$)
Zr-BEN	1.57	263	0.086	0.10
Al-BEN	1.73	335	0.156	0.08
Al-LAP	–	467	0.140	0.24

¹ volume estimated using the α_s method (Gregg and Sing, 1982) and employing, as a standard isotherm, the data obtained in a non-porous collapsed clay (Pires *et al.*, 1997)

² Volume estimated subtracting the value of V_{micro} from the total porosity volume

of this curve does not follow the same pattern as those obtained with pillared clays prepared from the BEN clay. In fact, the isotherms obtained show that the fundamental microporous nature of the samples as characterized by an initial step rise in the origin, followed by a long flat branch with an upwards deviation, indicate the presence of mesoporosity, whereas the curve displayed in Figure 1, typically an isotherm of type IV (Gregg and Sing, 1982), with a notorious hysteresis loop, shows that besides a microporous structure, Al-LAP also has a considerable volume of mesopores. This difference in the textural properties probably arises from the small dimensions of the crystals which promote a particular aggregation of the particles of this sample, edge-to-edge and edge-to-face, causing the formation of mesopores (Occelli *et al.*, 1984). The micro and mesopore volumes of the PILCs studied in this work are listed in Table 1. The micropore volume, V_{micro} , was evaluated using the α_s method (Gregg and Sing, 1982) and employing as standard isotherms the data obtained in a non-porous collapsed clay (Pires *et al.*, 1997) whereas the mesopore volume, V_{meso} , was estimated by subtracting the value of V_{micro} from the total porosity volume, determined from the amount of N_2 uptake at $p/p_0 = 0.95$, considered to be in the liquid state.

The N_2 adsorption isotherm obtained for the NaHY zeolite, not shown, was, as expected, similar to the curves characteristic of microporous materials. The micropore volume estimated from the application of the Dubinin-Radushkevich equation (Gregg and Sing, 1992) was $0.34 \text{ cm}^3 \text{ g}^{-1}$, in agreement with the values found in the literature for this type of zeolitic structure (Pires *et al.*, 1991) and so reveals the high crystallinity of the sample.

Acidity

Infrared spectroscopy of pyridine adsorbed on fresh samples. Infrared spectra in the $1400\text{--}1700 \text{ cm}^{-1}$ region of pyridine adsorbed on Al-BEN, Zr-BEN, Al-LAP and on the NaHY zeolite, after removing the physisorbed species, and those obtained after desorption at 200, 300 and 400°C are shown in Figure 2.

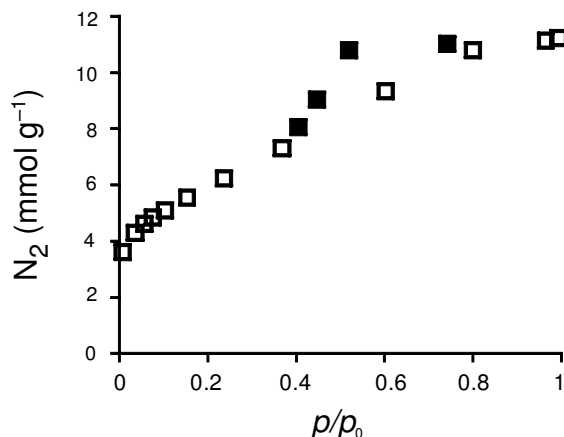


Figure 1. Nitrogen adsorption isotherm at -196°C on Al-LAP. Closed symbols are desorption points.

The IR spectra of adsorbed pyridine in all samples shows the presence of more or less intense bands around 1630 , 1550 , 1500 and 1450 cm^{-1} . The band at 1630 cm^{-1} is large, in fact it is a combination of two very close bands; the first at $1600\text{--}1620 \text{ cm}^{-1}$, attributed to pyridine adsorbed on Lewis acid sites, and the second at 1635 cm^{-1} , related to pyridine adsorbed on Brönsted acid sites. These two bands usually appear as a large band, so they are not used to distinguish the two types of acid sites. At 1500 cm^{-1} , a well defined band is found. The band corresponds to pyridine adsorbed at both Brönsted and Lewis acid sites, and so it cannot be used either to distinguish the two types of acid sites. The band localized at $1545\text{--}1555 \text{ cm}^{-1}$ is assigned to pyridine adsorbed on Brönsted acid sites and the band at $1445\text{--}1455 \text{ cm}^{-1}$ is attributed to pyridine adsorbed on Lewis acid sites (Hoff and Roelofsen, 1991). These last two bands are usually used to distinguish Brönsted and Lewis acid sites.

As expected, NaHY zeolite presents Lewis and Brönsted types of acid sites revealed by the intense bands at $1445\text{--}1455 \text{ cm}^{-1}$ and $1545\text{--}1555 \text{ cm}^{-1}$, respectively (marked as L and B in Figure 2).

The results obtained with pillared clays revealed that these samples present mainly Lewis acidity, as the band assigned to pyridine adsorbed on this type of acid site is well defined and stronger than that assigned to pyridine adsorbed on Brönsted acid sites, a result that is in agreement with the data published in the literature (*e.g.* Farfan-Torres *et al.*, 1991; Lambert and Poncelet, 1997). Moreover, the intensity of the band due to the pyridinium ion, negligible for Al oxide-pillared clays, is small but well defined for Zr-BEN, meaning that this sample presents a considerable number of Brönsted acid sites. On the other hand, these Brönsted sites are quite stable, as the intensity of the above-mentioned band remains practically constant after the sample was outgassed at 400°C . The presence of a significant number of Brönsted acid sites in PILCs is not common

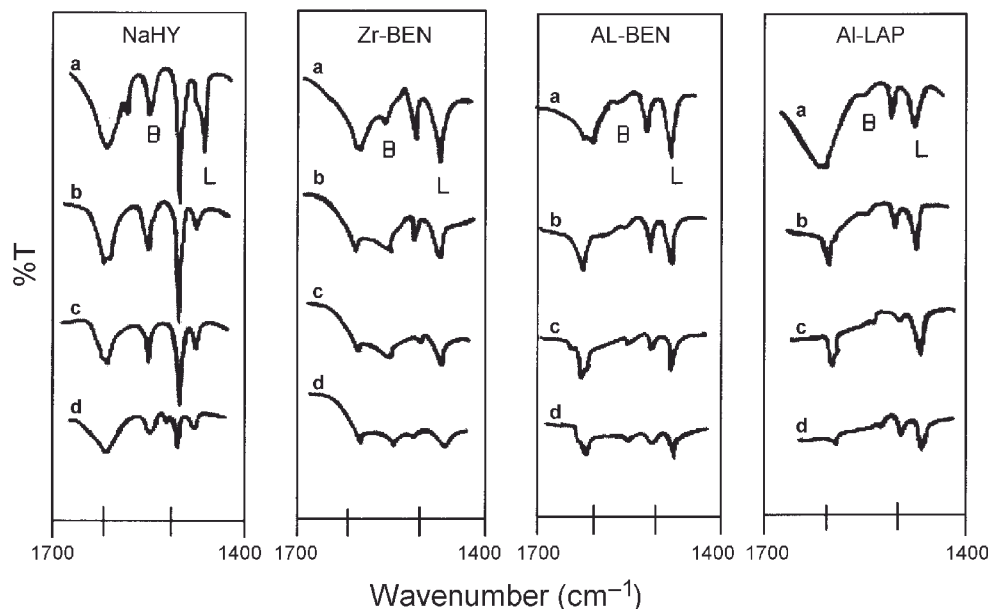


Figure 2. IR spectra of pyridine adsorbed at room temperature (a) and after outgassing at 200 (b), 300 (c) and 400°C (d), for all samples. B and L indicate the bands more related to Brönsted and Lewis acid sites, respectively.

but was found in other studies concerning Zr oxide-modified clays (Occelli, 1986; Farfan-Torres *et al.*, 1991, 1992). This important Brönsted acidity is interpreted as being the result of the presence of a positively charged amorphous hydrated zirconia phase that remains after calcination treatments.

For Lewis-type acidity, an estimate of the relative site population in the samples was attempted. To account for the differences due to density of samples and spectral path lengths of the wafers, the bands characteristic of pyridine coordinated to these acid sites were normalized against the structure Si-O combination band, at 1860–1800 cm^{-1} , which exists in different aluminosilicates such as clays and zeolites. Basila (1962) used this procedure in a study involving silica-alumina and more recently Bagshaw and Cooney (1993) and Pires *et al.* (1998b) also used this method in studies with pillared clays, but as far as we are aware, it has never been attempted when the characterization of zeolite acidity is of interest. Besides, it is important to note that in the present work the reproducibility of the method was proved using sub-samples of NaHY zeolite. The absorbances of the bands corresponding to pyridine adsorbed to Lewis acid sites were normalized by the absorbance of the structural band mentioned above. The values obtained, designated as $A_n(\text{Lewis})$ are shown in Figure 3 as a function of the desorption temperature. As can be seen, the samples studied can be ordered, in terms of their Lewis acid site density, in the following sequence:

$$\text{NaHY} \approx \text{Zr-BEN} > \text{Al-BEN} > \text{Al-LAP}$$

On the other hand, from this graphic representation it is also clear that, in general, Lewis acid sites are strong

enough to retain the pyridine adsorbed at 400°C, since no important variation in acid site density is detected when the desorption temperature is increased to this value. The exceptions are Zr-BEN and Al-LAP for which a small decrease in relative Lewis acid site populations is found after desorption treatments at 300 and 400°C, respectively.

Concerning the normalizing method used, it is interesting to note that from the results obtained in the present study this procedure can generally be applied to achieve a semi-quantitative estimate of the relative number of acid sites on an assemblage of aluminosilicates. Thus this method can be considered as an alternative to others proposed in the literature (Emeis, 1993), where quantification of acid sites is achieved using the molar extinction coefficient for the bands of adsorbed pyridine, knowing the weight of the wafers and assuming that they are homogeneous. In fact, an accurate determination of the weight of the wafers is often very difficult to obtain because of their fragility (and other

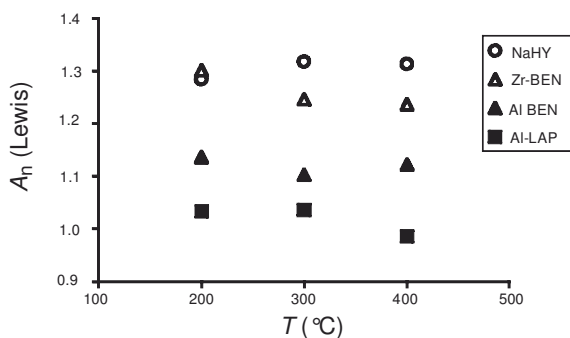


Figure 3. Normalized absorbances for pyridine adsorbed on Lewis sites, $A_n(\text{Lewis})$, vs. desorption temperature.

reasons), which prevents retention of their integrity throughout the experimental procedures, especially where pillared clays are concerned, and therefore the normalization against a structural band can be considered more advantageous.

Catalytic tests

For the 1-butene transformation over all samples, the same reaction parameters were maintained and three reaction temperatures, 130, 200 and 300°C were tested in order to see the temperature influence on the product distribution over PILCs and NaHY zeolite.

Activity and deactivation. In Figure 4 the deactivation curves for the 1-butene transformation at $T = 130^\circ\text{C}$ vs. time-on-stream for all solids are presented. The activity values were evaluated on the basis of the total reactant conversion. The initial activity, considered after 5 min, allows the establishment of the following sequence:

$$\text{NaHY} \approx \text{Zr-BEN} > \text{Al-BEN} \gg \text{Al-LAP}$$

As the figure shows, except for Al-LAP, all the samples have a great initial activity, especially the first two. In fact, Zr-BEN reveals an initial activity almost identical to that of the zeolite, but it is the sample where a more rapid deactivation is observed. This more pronounced deactivation probably reflects the existence of smaller micropores in the Zr-BEN sample as the lower d_{001} values are a first indication (Table 1). These narrow micropores are more easily obstructed with coke or coke precursors. From Figure 4 it is also clear that the pillared clay Al-LAP shows a much lower initial activity, though its deactivation is slower than that observed for the other samples, this being a consequence of its delaminated nature, the cause of the mesopores. These findings indicate the important role of the porous structure in the catalytic behaviour of these solids. In fact, it is well known that the three-dimensional circulation in the NaHY zeolite porous network and the two-dimensional circulation in the pillared clays porous system is an important factor that affects the selectivity of the reaction products.

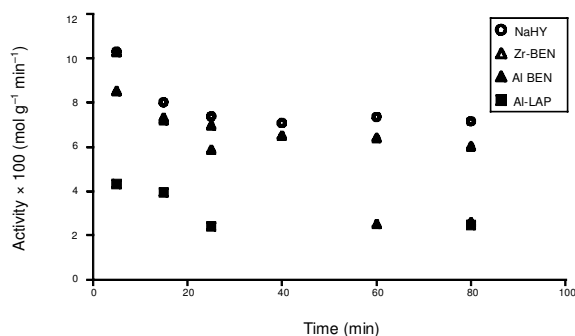


Figure 4. Deactivation curves for the 1-butene transformation at $T = 130^\circ\text{C}$.

Influence of the reaction time. To show the influence of the time-on-stream on the predominant reactions, and consequently on the respective reaction products, Figure 5 shows three histograms with the product distribution at three different reaction times, for 130°C.

At the beginning of the reaction (5 min) a wide dispersion of the products was observed. These were formed as a result of isomerization (*cis*- and *trans*-2-butene) and of oligomerization reactions followed by cracking in small fragments (C_1 , C_2 , C_3) and also longer fragments (C_7 or even $>C_7$). Traces of hydrogen transfer products, namely iso-butane, are also detected as secondary products. According to Xu *et al.* (1994), these products result from a reaction between iso-butene

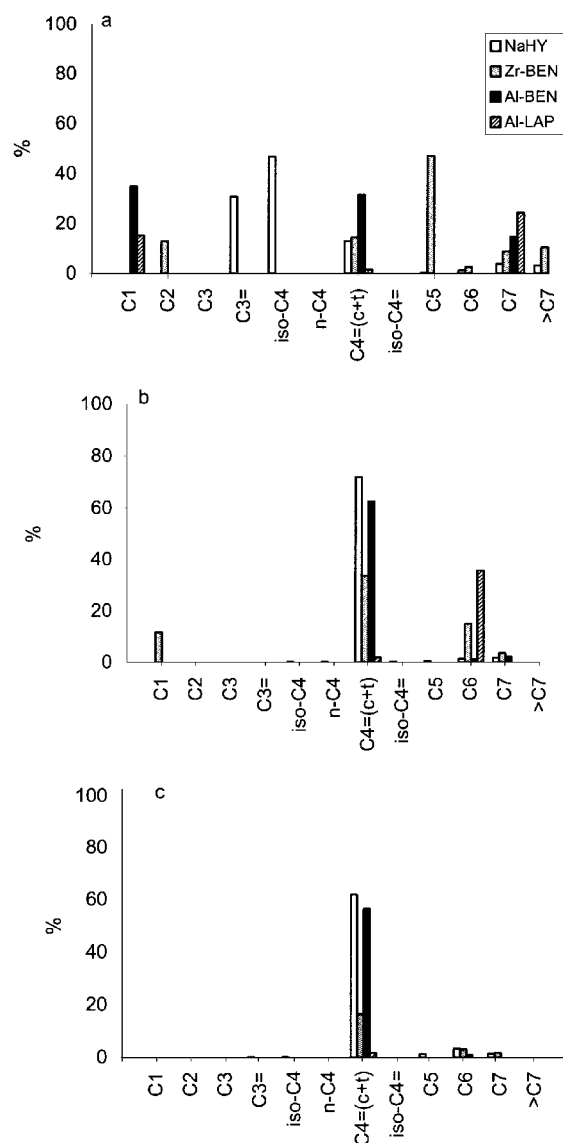


Figure 5. Product distribution for the 1-butene transformation at $T = 130^\circ\text{C}$ for (a) 5 min; (b) 15 min and (c) 80 min of time-on-stream.

and hydrogen, arising from the formation of aromatic products, justifying the absence of iso-butene in the product range. The dispersion in the products can be explained by the high activity of the fresh catalysts, almost all the acid sites being active.

After 15 min of reaction, the product distribution shows clearly that linear isomerization is the main reaction, producing the *cis*- and *trans*-2-butene isomers. This behavior can be explained by the previous deactivation of the most acidic sites by coke deposition, followed by the prevalence of the reaction that needs lower acidity. Additionally, the coke deposited decreases the effective pore diameter, favoring in this way the production of less bulky molecules. This process is confirmed with the results of the histogram corresponding to the 80 min reaction time of where only the linear isomers *cis*- and *trans*-2-butene were found.

For all the samples studied, the product distribution, as a function of time-on-stream, obeys a common pattern for the three temperatures, except for Al-LAP. In fact, this material shows an abnormal behavior for all the studied temperatures, with high percentages of isomerization products after 5 min of reaction time, and significant quantities of oligomerization products after 15 min of reaction. This behavior can be related to the lower acidity of Al-LAP and also attributed to the type of aggregation of Laponite particles, leading to the formation of mesoporosity, which does not occur in either the zeolite or in the smectites studied.

Influence of temperature. For an identical reaction time (15 min) a similar set of reaction products is observed for all the studied temperatures, *i.e.* isomerization, oligomerization, cracking and traces of hydrogen transfer products. For 130°C the isomerization products constitute a large majority and for the highest temperatures, a mixture ranging from methane and ethane to heptane is observed, showing that for these temperatures (200 and 300°C), besides isomerization and hydrogen transfer there is an increase in the products resulting from the oligomerization followed by cracking, as found by Kissin (1996).

***Cis/trans*-2-butene ratio.** As stated in the literature, the linear isomerization of olefins is one way to evaluate the catalyst global acidity. In the particular case of 1-butene isomerization, this evaluation is based on the ratio of the linear isomers *cis*- and *trans*-2-butene (Foster and Cvetanovic, 1959; Tsuchiya *et al.*, 1987).

As was stated by Foster and Cvetanovic (1959), the production of *cis*- and *trans*-2-butene in a concentration ratio near one reveals the presence of acidic solids. In fact, the value of the *cis/trans* linear isomers ratio was used by other authors to obtain information on the total acidity of pillared clays (Geatti *et al.*, 1997) and zeolites (Tsuchiya *et al.*, 1987). As the pore dimensions of the pillared clays (Zr-BEN and Al-BEN) and NaHY zeolite

are very similar, the preferential formation of *cis*- or *trans*-2-butene can be attributed to the differences in the global acidity of these solids. In Figure 6 the evolution of the *cis/trans* ratio in terms of the time-on-stream is shown for all samples, and for a temperature reaction of 130°C. As can be seen, all the samples promote the formation of both isomers in approximately the same proportion, which indicate, as mentioned, the acidic character of all these solids. In fact, NaHY zeolite, Al-BEN and Zr-BEN present a *cis/trans* ratio very close to one. Al-LAP has a slightly larger *cis/trans* ratio, indicating that this pillared clay is less acidic than the other studied samples. It is very important to note the fact that NaHY zeolite and Zr-BEN show an evolution of the *cis/trans* ratio (Figure 6) practically coincident all along the reaction time, which means that these materials have an identical global acidity, which is in total agreement with the results of the pyridine adsorption discussed previously. The *cis/trans* ratio deviation from unity at the beginning of the reaction, must be correlated with the smaller quantity of isomers formed at this reaction time which probably leads to a large error in its calculation.

It is important to state that the identification of the type of acid site responsible for the acidity is impossible to recognize in any catalytic study. So, with catalytic results one can only discuss the overall acidity. However, the correlation between a catalytic study and an IR spectroscopy study of pyridine adsorbed on deactivated samples can allow some interesting correlations, or even conclusions explained in the following point.

Infrared spectroscopy of pyridine adsorbed on deactivated samples

Despite the considerable number of studies concerning the reaction mechanism of olefins transformation over acidic catalysts, this is still a controversial theme. Some authors agree that the reactions take place only on Brönsted acid sites (Dunning, 1953; Weeks *et al.*, 1974), while the results obtained in other studies suggest that Lewis acid sites can act in cooperation with Brönsted acid sites (Jacobs *et al.*, 1975) or even isolated from them

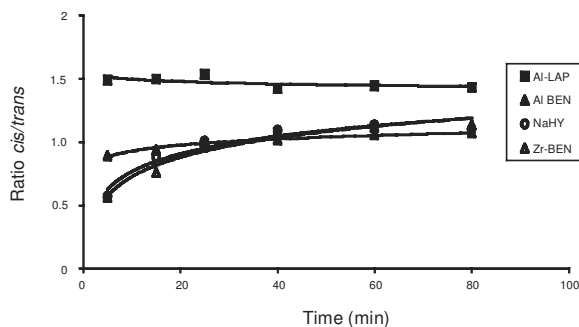


Figure 6. *Cis/trans* 2-butene ratio vs. time-on-stream at T = 130°C.

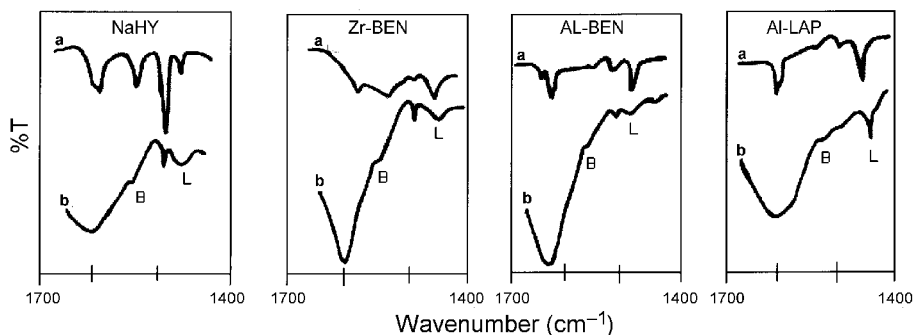


Figure 7. IR spectra of pyridine adsorbed on fresh samples after desorption treatment at 300°C (a) and on deactivated samples after 1-butene transformation at $T = 300^{\circ}\text{C}$ (b).

(Ballivet *et al.*, 1974; Datka, 1981a,b), Perot *et al.* (1976), Guisnet *et al.* (1977) and Datka (1981b), also indicate that the Lewis sites are the centers responsible for the oligomerization and linear isomerization of olefins. It is important to bear in mind that all these studies were with zeolites where the acidity is predominantly of Brønsted type. In PILCs that have mainly Lewis acidity, the remarks about which type of acid sites are involved in olefin reactions are not necessarily valid.

To answer this question, different approaches can be taken, *e.g.* analysis by adsorption of pyridine, of the type of acid sites present on fresh and on deactivated samples. As far as we know, this method was followed only by Auer and Hofmann (1993) who studied adsorption of pyridine on pillared clays used in toluene disproportionation, concluding, in this case, that both Brønsted and Lewis sites are involved.

In the present work, still with the aim of exploring which type of PILC acid sites are involved in 1-butene reactions, the IR spectra of pyridine adsorbed on the acid sites of the deactivated samples after the catalytic tests, performed at 300°C, were recorded. These spectra were compared with those obtained from fresh samples after desorption treatment at the same temperature. It was assumed that the decrease in the intensity of the band assigned to pyridine interaction with acid sites is due to poisoning of the acid sites by the coke formed during the catalytic reaction.

Figure 7 shows the IR spectra for all the samples. In all cases, the band related to Lewis acid sites continues to be present after the catalytic reaction, although its intensity always decreases. From these results, it can be concluded that Lewis acid sites act like active sites during the catalytic transformation of 1-butene. This explains the good correlation between the two methods for characterization of acidity used in this study. In fact, the ordering of the samples obtained considering the normalized absorbance values ($A_n(\text{Lewis})$) coincides with that based on the values of the initial catalytic activity of 1-butene transformation.

On the other hand, for samples that initially present relatively well defined bands assigned to pyridine adsorbed on Brønsted acid sites, namely NaHY zeolite

and Zr-BEN, it is interesting that, after the reaction these bands practically disappear, indicating that Brønsted sites intervene in the catalytic reactions. The global nature of our results shows that in pillared clays, as in zeolites, Brønsted and Lewis acid sites are active for 1-butene transformation.

CONCLUSIONS

The results of the characterization of acidity of a set of pillared clays and a NaHY zeolite by pyridine adsorption followed by IR spectroscopy and 1-butene catalytic transformation reveal that these two techniques allow us to compare the surface acidic properties of the samples. As was expected, pillared clays show mainly Lewis-type acidity, though Zr-BEN, the pillared clay most like the NaHY zeolite, showed a significant Brønsted acidity.

With regard to Lewis acidity, it must be emphasized that a new method was used to normalize the intensity of the IR bands, giving a sequence of sample acidity which correlates well with the respective catalytic activities.

The two characterization methods were used in a complementary way by determining the IR spectra of pyridine adsorbed on the samples before and after the catalytic tests. The results show that, in all samples, Lewis acid sites have an active role in the catalytic transformation of 1-butene. In samples with Brønsted acid sites, their role as active sites in this catalytic reaction was also demonstrated.

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REFERENCES

- Araya, A., Blake, A.J., Blake, J., Harrison, I.D., Leach, H.F., Lowe, B.M., Whan, D.A. and Collins, S.P. (1992) Synthesis, properties, and catalytic behaviour of zeolite EU-12. *Zeolites*, **12**, 24–31.
- Auer, H. and Hofmann, H. (1993) Pillared clays: characteriza-

- tion of acidity and catalytic properties and comparison with some zeolites. *Applied Catalysis. A: General*, **97**, 23–38.
- Bagshaw, S.A. and Cooney, R.P. (1993) FTIR surface site analysis of pillared clays using pyridine probe species. *Chemistry of Materials*, **5**, 1101–1109.
- Ballivet, D., Barthomeuf, D. and Trambouze, Y. (1974) The isomerization of cis-2-butene over silica-alumina catalysts. III. Dependence on alumina content. *Journal of Catalysis*, **35**, 359–362.
- Basila, M.R. (1962) An infrared study of a silica-alumina surface. *The Journal of Physical Chemistry*, **66**, 2223–2228.
- Benito, I., del Riego, A., Martínez, M., Blanco, C., Pesquera, C. and González, F. (1999) Toluene methylation on Al₁₃- and GaAl₁₂-pillared clay catalysts. *Applied Catalysis A: General*, **180**, 175–182.
- Brotas de Carvalho, M., Pires, J. and Carvalho, A.P. (1996) Characterization of clays and aluminium pillared clays by adsorption of probe molecules. *Microporous Materials*, **6**, 65–77.
- Cool, P. and Vansant, E.F. (1996) Preparation and characterization of zirconium pillared laponite and hectorite. *Microporous Materials*, **6**, 27–36.
- Costa, C., Lopes, J.M., Lemos, F. and Ramôa Ribeiro, F. (1999) Activity-acidity relationship in zeolite Y. Part 1. Transformation of light olefins. *Journal of Molecular Catalysis A: Chemical*, **144**, 207–220.
- Datka, J. (1981a) Transformations of butanes on dehydroxylated Y zeolites studied by infrared spectroscopy. *Journal of Chemical Society Faraday Transactions 1*, **77**, 2633–2643.
- Datka, J. (1981b) Adsorption of butanes on NaY and dehydroxylated Y zeolites by infrared spectroscopy. *Journal of Chemical Society Faraday Transactions 1*, **77**, 1309–1314.
- Dunning, H.N. (1953) Review of olefin isomerization. *Industrial and Engineering Chemistry*, **45**, 551–564.
- Emeis, C.A. (1993) Determination of integrated molar extinction coefficients for infrared absorption bands of pyridine adsorbed on solid acid catalysts. *Journal of Catalysis*, **141**, 347–354.
- Farfan-Torres, E.M., Dodeycker, O. and Grange, P. (1991) Zirconium pillared clays. Influence of basic polymerization of the precursor on their structure and stability. Pp. 337–343 in: *Preparation of Catalysts V* (G. Poncelet, P.A. Jacobs, P. Grange and B. Delmon, editors). Elsevier Science Publishers, Amsterdam.
- Farfan-Torres, E.M., Sham, E. and Grange, P. (1992) Pillared clays: preparation and characterization of zirconium pillared montmorillonite. *Catalysis Today*, **15**, 515–526.
- Flego, C., Galasso, L., Millini, R. and Kiricsi, I. (1998) The influence of the composition on the thermal and acid characteristics of multi-component oxide pillared montmorillonite. *Applied Catalysis A: General*, **168**, 323–331.
- Foster, N.F. and Cvetanovic, R.J. (1959) Stereoselective catalytic isomerization of n-butenes. *Journal of American Chemical Society*, **82**, 4274–4277.
- Geatti, A., Lenarda, M., Storaro, L., Ganzerla, R. and Perissinotto, M. (1997) Solid acid catalysts from clays: cumene synthesis by benzene alkylation with propene catalyzed by cation exchanged aluminum pillared clays. *Journal of Molecular Catalysis A: Chemical*, **121**, 111–118.
- Gil, A., Gandía, L.M. and Vicente, M.A. (2000) Recent advances in the synthesis and catalytic applications of pillared clays. *Catalysis Reviews – Science and Engineering*, **42**, 145–212.
- Gregg, S.J. and Sing, K.S.W. (1982) *Adsorption, Surface Area and Porosity*, Academic Press, London, pp. 209–228.
- Guisnet, M., Lambert, J.L., Perot, G. and Mauriel, R. (1977) Catalytic isomerization of ethylenic hydrocarbons. XIV. Effect of drying and reaction temperature on the isomerization of deuterated butenes over alumina. *Journal of Catalysis*, **48**, 166–176.
- Guiu, G. and Grange, P. (1997) Tantalum pillared montmorillonite. II. Acidic and catalytic properties. *Journal of Catalysis*, **168**, 463–470.
- Hooff, J.H.C. and Roelofs, J.W. (1991) Techniques of zeolite characterization. Pp. 241–283 in: *Introduction to Zeolite Science and Practice* (H. van Bekkum, E.M. Flaningan and J.C. Jansen, editors). Elsevier Science Publishers, Amsterdam.
- Jacobs, P.A., Declerck, L.J., Vandamme, L.J. and Uytterhoven, P. (1975) Active sites in zeolites. Part 4. n-butene isomerization over deammoniated and partly hydrolysed NH₄Y. *Journal of the Chemical Society, Faraday Transactions*, **71**, 1545–1552.
- Kissin, Y.V. (1996) Chemical mechanism of hydrocarbon cracking over solid acidic catalysts. *Journal of Catalysis*, **163**, 50–62.
- Ladavos, A.K., Trikalitis, P.N. and Pomonis, P.J. (1996) Surface characteristics and catalytic activity of Al-pillared (AZA) and Fe-Al-pillared (FAZA) clays for isopropanol decomposition. *Journal of Molecular Catalysis*, **106**, 241–254.
- Lambert, J.F. and Poncelet, G. (1997) Acidity in pillared clays: origin and catalytic manifestations. *Topics in Catalysis*, **4**, 43–56.
- Malla, P. and Komarneni, S. (1990) Synthesis of highly microporous hydrophilic alumina-pillared montmorillonite: Water-sorption properties. *Clays and Clay Minerals*, **38**, 363–372.
- Medema, J. (1975) Isomerization of butene over alumina. *Journal of Catalysis*, **37**, 91–100.
- Molina, R., Schutz, A. and Poncelet, G. (1994) Transformation of m-xylene over Al-pillared clays and ultrastable zeolite Y. *Journal of Catalysis*, **145**, 79–85.
- Occelli, M.L. (1986) New routes to the preparation of pillared montmorillonite catalysts. *Journal of Molecular Catalysis*, **35**, 377–389.
- Occelli, M.L., Landau, S.D. and Pinnavaia, T.J. (1984) Cracking selectivity of a delaminated clay catalyst. *Journal of Catalysis*, **90**, 256–260.
- Pereira, P.R., Pires, J. and Brotas de Carvalho, M. (1998) Zirconium pillared clays for carbon dioxide/methane separation. 1. Preparation of adsorbent materials and pure gas adsorption. *Langmuir*, **14**, 4584–4588.
- Perot, G., Guisnet, M. and Mauriel, R. (1976) Catalytic isomerization of ethylenic hydrocarbons. *Journal of Catalysis*, **41**, 14–21.
- Pires, J., Carvalho, M.B., Ribeiro, F.R. and Derouane, E.G. (1991) Textural characteristics of Y and ZSM-20 zeolites determined by nitrogen adsorption. *Zeolites*, **11**, 345–348.
- Pires, J., Carvalho, M.B. and Carvalho, A.P. (1997) Aluminium-pillared clays: decomposition of the intercalating species and textural properties. *Zeolites*, **19**, 107–113.
- Pires, J., Machado, M. and Brotas de Carvalho, M. (1998a) Porosity and thermal stability of PILCs prepared with clays from different origins and different metal-polyhydroxycationic species of Al and Al/Ce. *Journal of Materials Chemistry*, **8**, 1465–1469.
- Pires, J., Carvalho, A.P., Pereira, P.R. and Brotas de Carvalho, M. (1998b) Acidity studies on pillared clays (PILCs) by pyridine adsorption and 1-butanol dehydration. *Reaction Kinetics and Catalysis Letters*, **65**, 9–15.
- Pires, J., Brotas de Carvalho, M., Carvalho, A.P., Guil, J.M. and Perdigón-Melón, J.A. (2000a) Heats of adsorption of n-hexane by thermal gravimetry with differential scanning calorimetry (TG-DSC): a tool for textural characterization of pillared clays. *Clays and Clay Minerals*, **48**, 385–391.
- Pires, J., Carvalho, A.P., Clara, E. and Brotas de Carvalho, M.

- (2000b) Adsorção de Compostos Orgânicos Voláteis (VOCs). *XVII Ibero American Symposium on Catalysis, Porto*, p. 651.
- Pires, J., Carvalho, A. and Carvalho, M.B. (2001) Adsorption of volatile organic compounds in Y zeolites and pillared clays. *Microporous and Mesoporous Materials*, **43**, 277–287.
- Raimond, M., De Stefanis, A., Perez, G. and Tomlinson, A.A.G. (1998) PLS vs. Zeolites as sorbents and catalysts. 5. Evidence for Brønsted/Lewis acid crossover and high acidity in conversions of C_{1–3} alcohols in some alumina-pillared smectite clays. *Applied Catalysis A: General*, **171**, 85–97.
- Tsuchiya, S., Kawasaki, S., Mikami, M. and Imamura, H. (1987) Reaction profile of isomerization of n-butenes over zeolite catalysts. *Zeolites*, **7**, 4–6.
- Vaughan, D.E.W. (1988) Pillared clays, a historical perspective. Pp. 187–198 in: *Pillared Clays: Catalysis Today* (R. Burch, editor). Elsevier, Amsterdam.
- Weaver, C.E. and Pollard, L.D. (1975) *The Chemistry of Clay Minerals*. Elsevier, Amsterdam, pp. 55–86.
- Weeks, Jr., T.J., Angell, C.L., Ladd, I.R. and Bolton, A.P. (1974) The polymerisation and aromatic alkylation of butene-1 with calcined ammonium type Y zeolite. *Journal of Catalysis*, **33**, 256–264.
- Xu, X.Q., Yin, Y.G., Suib, S.L. and Young, C.L. (1994) Selective conversion of n-butene to isobutylene at extremely high space velocities on ZSM-23 zeolites. *Journal of Catalysis*, **150**, 34–45.

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